



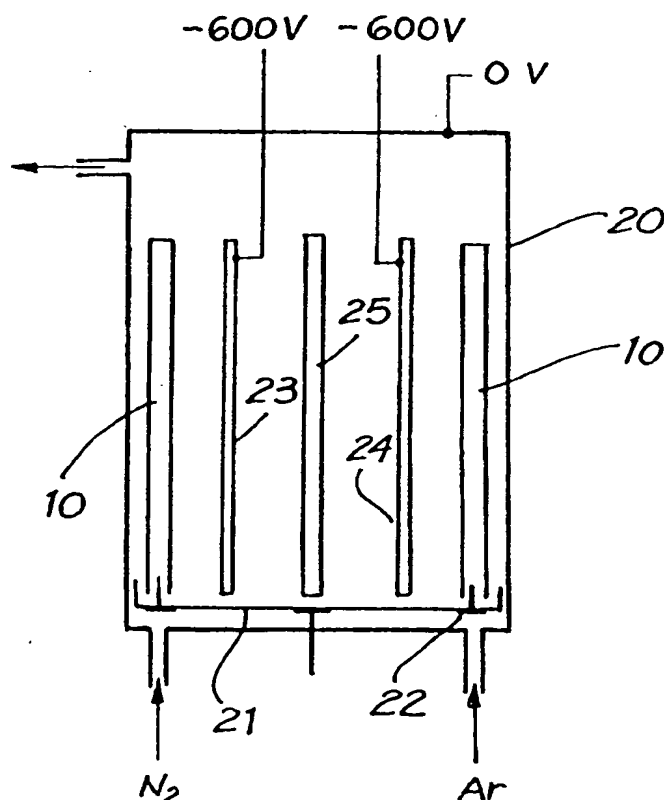
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 14/06, 14/08, 14/34, 14/35, 14/36		A1	(11) International Publication Number: WO 97/00335
			(43) International Publication Date: 3 January 1997 (03.01.97)
(21) International Application Number: PCT/AU96/00363 (22) International Filing Date: 18 June 1996 (18.06.96) (30) Priority Data: PN 3641 19 June 1995 (19.06.95) AU (71) Applicant (for all designated States except US): THE UNIVERSITY OF SYDNEY [AU/AU]; Parramatta Road, Sydney, NSW 2006 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): ZHANG, Qi-Chu [CN/AU]; The University of Sydney, Dept. of Applied Physics, Parramatta Road, Sydney, NSW 2006 (AU). MILLS, David [AU/AU]; The University of Sydney, Dept. of Applied Physics, Parramatta Road, Sydney, NSW 2006 (AU). (74) Agent: GRIFFITH HACK & CO.; G.P.O. Box 4164, Sydney, NSW 2001 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.	

(54) Title: SOLAR SELECTIVE SURFACE COATING

(57) Abstract

A solar selective surface coating (13) that is deposited on a solar collector element (10). The surface coating (13) comprises a three-layer structure having an inner layer (14) in the form of a bright metal infrared reflective coating layer, a solar energy absorptive coating layer (15) deposited on the reflective coating layer, and an anti-reflective surface layer (16). The absorptive coating (15) is deposited as a cermet, typically a tungsten-aluminium nitride cermet, which is formed by sputtering material simultaneously from first and second metal electrodes (23 and 24) in the presence of a gas which is reactive with the metal from which the second electrode (24) is formed and substantially non-reactive with the metal from which the first electrode (23) is formed. That is, the solar energy absorptive coating (15) is formed by co-depositing materials from the first and second electrodes (23 and 24) in the presence of a gas which is reactive with the metal of one only of the electrodes.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SOLAR SELECTIVE SURFACE COATINGFIELD OF THE INVENTION

This invention relates to a solar selective surface coating, to a method of depositing such coating on a substrate and to a collector element for use in a solar energy collector system.

BACKGROUND OF THE INVENTION

Most solar selective surface coatings currently employ metal-dielectric composites (which are known as cermet) as absorbers of solar energy. When deposited with appropriate layer thicknesses and metal volume fractions, the composites exhibit strong absorptive peaks in the main solar radiation region whilst remaining substantially transparent to thermal (infrared) radiation. The composites are deposited on infrared reflecting metal bases to form solar selective surface coatings.

Absorptive coatings that have been studied include direct current (dc) reactively sputtered chromium-oxygen, chromium-nitrogen, chromium-carbon, titanium-nitrogen, titanium-carbon, titanium-nitrogen-carbon, zirconium-nitrogen, zirconium-nitrogen-carbon, nickel-carbon, nickel-nitrogen, molybdenum-carbon, stainless steel-carbon and aluminium-nitrogen composites. Several of these composites have been employed as absorptive coatings on commercially produced collector elements, including dc reactively sputtered stainless steel-carbon and aluminium-nitrogen composites. However these composite coatings can be used only at low temperatures or at medium temperatures (up to about 350°C) because of their lack of thermal stability at high temperatures.

Absorptive coatings that do exhibit stability at higher temperatures include radio frequency (rf) sputtered metal- Al_2O_3 and metal- SiO_2 composites. Cermet material absorptive coatings that have been employed in commercially produced collector elements have been deposited as composites of dc sputtered Mo metal and rf sputtered Al_2O_3 and SiO_2 dielectric materials.

However, cermet coatings that employ rf sputtered dielectric materials are expensive to produce, both in terms of capital equipment and energy required for deposition. Also, difficulty is encountered in
5 depositing cermets because of the potential of the dielectric material targets to crack due to poor thermal conductivity.

SUMMARY OF THE INVENTION

The present invention seeks to provide a solar
10 selective surface coating which incorporates a cermet absorptive layer, which is produced by a relatively economical deposition process and which, when incorporating an appropriate metal fraction in the cermet, exhibits high temperature thermal stability.

15 Thus, the present invention may be defined broadly as providing a solar selective surface coating that comprises an infrared reflective metal and a solar energy absorptive coating deposited on the reflective metal. The absorptive coating comprises a cermet which is formed
20 by sputtering material simultaneously from first and second metal electrodes onto the reflective metal in the presence of at least one gas that is reactive with the metal from which the second electrode is formed and substantially non-reactive with the metal from which the
25 first electrode is formed.

The invention may be defined also as providing a method of forming a solar selective surface coating and which comprises the steps of:

- 30 (a) depositing an infrared reflective metal layer on a substrate by a non-reactive sputtering process, and
(b) depositing a solar energy absorptive coating on the reflective metal layer.

The absorptive coating is deposited as a cermet which is formed by sputtering material simultaneously from first
35 and second metal electrodes onto the reflective metal layer in the presence of at least one gas which is reactive with the metal from which the second electrode

is formed and substantially non-reactive with the metal from which the first electrode is formed.

5 The invention also provides a solar collector element that comprises a tube through which a heat exchange fluid may be passed, a glass envelope surrounding the tube, an evacuated space defined by the tube and the envelope, and a solar selective surface coating as above defined deposited on the outer surface of the tube.

10 The tube of the solar collector element may be formed from metal or glass, and when formed from an appropriate metal the outer surface of the tube may constitute the infrared reflective layer of the solar selective surface coating. That is, in certain
15 circumstances the solar absorptive coating may be deposited directly onto the outer surface of the collector element heat exchange tube.

The various forms of the present invention as above defined are characterised by a common feature, namely the
20 co-deposition of materials from the first and second electrode metals in the presence of a gas which is reactive with the metal of one only of the electrodes.

PREFERRED FEATURES OF THE INVENTION

25 The gas which is selected to provide for reactive sputtering of the cermet will be determined by the metals from which the first and second electrodes are formed. As indicated previously, the gas must be reactive with the second electrode metal, to form the dielectric component of the cermet, and substantially non-reactive
30 with the first electrode metal. The gas may comprise a gas mixture (i.e., a mixture of two or more reactive gases) in an inert sputter supporting gas such as argon, but the reactive gas most preferably comprises nitrogen. When sputtering in the presence of nitrogen, oxygen may
35 with advantage be absorbed in reactive sputtering of the second electrode metal to form the dielectric component.

When sputtering in the presence of nitrogen reactive gas, the metal which forms the metallic component of the

cermet (i.e., the first electrode metal as referred to above) is preferably selected from tungsten, tungsten based alloys, stainless steel, nickel, nickel based alloys such as Inconel, Hastelloy and Monel, nickel-
5 chromium alloys, platinum, iridium, osmium, ruthenium, rhodium, rhenium, molybdenum, molybdenum based alloys and gold. However, the first electrode metal most preferably comprises tungsten, particularly for applications where
10 the absorptive coating is required to exhibit high temperature thermal stability.

When sputtering in the presence of oxygen reactive gas, the (first electrode) metal which forms the metallic component of the cermet is preferably selected from platinum, iridium, ruthenium, rhodium, rhenium and gold.
15 However, in this case the first electrode metal most preferably comprises gold to minimise cost or platinum to maximise high temperature stability.

The metal which is reactively deposited to form the dielectric matrix (i.e., the second electrode metal as referred to above) is preferably selected from magnesium
20 and aluminium. However, the second metal most preferably comprises aluminium in the interest of minimising cost.

The infrared reflective metal preferably is selected from aluminium, tungsten, copper, gold, silver and
25 molybdenum. However, tungsten and molybdenum are most preferred for selective surface coatings that are required to operate at high temperature.

Deposition of the various metals, including non-reactive sputtering of the infrared reflective layer and
30 co-deposition of the first and second metals in the presence of the reactive gas, is effected by direct current (dc) or alternating current (ac) magnetron sputtering. Radio frequency (rf) magnetron sputtering could be employed but the economic advantage of the
35 present invention would then be lost or, at least, significantly diminished.

The absorptive coating may be deposited as a substantially homogeneous cermet, that is with the metal

fraction uniformly distributed throughout the dielectric matrix for the full thickness of the coating. Alternatively, the absorptive coating may be graded, such that the metal fraction of the cermet increases with
5 depth of the coating. As a further alternative, the absorptive coating may comprise a multi-layer cermet coating, each cermet layer being substantially homogeneous but each layer having a refractive index which is different from the or each adjacent layer.
10 Also, each layer will have a thickness which is substantially transparent to infrared radiation but which provides for absorption of solar radiation by internal absorption and phase cancellation interference.

A preferred form of multi-layer absorptive coating
15 comprises a two-layer cermet structure. The refractive index mismatch between the two adjacent layers may then be achieved by use of different cermet materials in the respective layers. However, it is preferred that the cermet component materials be the same in each layer and
20 that the refractive index mismatch be achieved by depositing different metal volume fractions in adjacent layers. Again in the case of a two-layer absorptive coating, it is preferred that the inner layer be constituted by a high metal volume fraction cermet and
25 that the outer layer be constituted by a low metal volume fraction cermet.

Whatever may be the structure of the absorptive surface coating, it is preferred that an anti-reflection surface be deposited upon the absorptive coating. The
30 anti-reflective surface will be composed of a transparent dielectric material which enhances solar absorption and, in the case of the preferred form of the invention which comprises a W-AlN composite, the anti-reflection material will preferably be composed of reactively sputtered
35 aluminium nitride, aluminium oxide or aluminium oxynitride.

An anti-diffusion layer may optionally be deposited between the absorptive coating and the infrared

reflective layer and/or between the infrared reflective layer and the substrate in the complete solar selective surface coating. Also, an adhesion layer may optionally be deposited between the infrared reflective layer and the substrate.

The invention will be more fully understood from the following description of a preferred embodiment of a solar selective surface coating and a method of depositing such coating on an all-glass tubular solar collector element. The description is provided with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings -

Figure 1 shows an elevation view of a collector element,

Figure 2 shows on a very much enlarged scale a portion of the surface coating upon a part of the collector element,

Figure 3 shows a diagrammatic representation in elevation of a sputtering chamber in which deposition of the surface coating is effected, and

Figure 4 shows a plan view of the chamber that is illustrated in Figure 3.

DETAILED DESCRIPTION OF THE INVENTION

As illustrated in Figure 1, the collector element comprises an inner single-ended glass tube 10 which typically has an internal diameter in the order of 30 mm and an axial length in the order of 1000 to 2000 mm. The tube 10 is located within and is end-sealed to an outer glass tube 11, and the space 12 between the two tubes is evacuated. A thin film solar selective surface coating 13 is deposited on the outer surface of the inner tube 10.

The collector element would normally be mounted within a concentrator (not shown) and be connected in fluid circuit communication with a bank of similar elements. A heat exchange fluid is channelled into the inner tube 10 by way of a manifold (not shown), and

thermal energy derived by absorption of solar radiation is conducted through the wall of the inner tube 10 to effect heating of the exchange fluid.

The surface coating 13 is illustrated in Figure 2 and comprises a three-layer structure. The inner layer 14 comprises an infrared reflective metal which is composed of a bright metal selected from those previously mentioned but which preferably comprises tungsten or molybdenum where the selective surface coating is to be operated at a high temperature. The infrared reflective layer is deposited by a dc magnetron sputtering process, to be hereinafter described, to a thickness in the range of 100 to 400 nm and preferably to a thickness of about 300 nm. By depositing the reflective layer to such a thickness, infrared reflectance is enhanced.

The reflective layer 14 may be deposited as two sub-layers, one being an anti-diffusion layer or an adhesion layer.

A solar energy absorptive coating 15 is deposited as a cermet on the infrared reflective layer 14. The cermet layer 15 is deposited to a thickness which is substantially transparent to infrared radiation but which facilitates absorption of solar radiation by internal absorption and phase cancellation interference. Thus, the cermet layer 15 has a thickness within the range 40 to 160 nm and preferably within the range 60 to 140 nm.

The cermet absorptive coating layer 15 comprises a composite of tungsten metal (W) and an aluminium nitride (AlN) dielectric, and the cermet is established by co-depositing material simultaneously from two metal electrodes, one of which is formed from tungsten and the other of which is formed from aluminium. The deposition is effected by a sputtering process in the presence of nitrogen gas. The nitrogen does not react significantly with the tungsten but does react strongly with the aluminium to form aluminium nitride during the sputtering process.

An anti-reflection surface layer 16 is deposited upon the absorptive coating 15 and is constituted by a transparent dielectric material which functions to enhance solar absorption. The surface layer 16 conveniently comprises reactively sputtered aluminium nitride but it might also comprise aluminium oxide or aluminium oxynitride, and the surface layer is typically deposited to a thickness in the range 60 to 100 nm.

The complete surface coating as illustrated in Figure 2 may be deposited in the sputtering chamber as shown diagrammatically in Figures 3 and 4.

As illustrated in Figures 3 and 4, the sputtering chamber comprises a generally cylindrical chamber 20 in which a rotatable carrier 21 is located. The carrier is driven to rotate about the central axis of the chamber 20 with an angular velocity which is selectively variable within the range 3 to 10 revolutions per minute (rpm). The carrier 21 supports a plurality of the glass tubes 10 on which the selective surface coating 13 is to be deposited and each of the tubes is supported by a rotatable mandrel 22 which is driven to cause the tube to rotate about its own axis with an angular velocity in the range 30 to 70 rpm. The tubes 10 are positioned around the circumference of a circle having a diameter in the order of 1000 mm and the chamber 20 has a height sufficient to receive the 1000 to 2000 mm long tubes.

Two tubular metal target electrodes 23 and 24 are positioned diametrically about the centre axis of the sputtering chamber 20 and extend parallel to the axis of the chamber. The two electrodes are separately and selectively connected as cathodes to a power supply (not shown) and when so connected are maintained at a potential in the order of -600 volts. The wall of the chamber 20 is connected to the power supply to form an anode and is maintained at a potential of +600 volts relative to the cathodes, that is at earth (zero) potential.

Although not shown in Figures 3 and 4, the tubular target electrodes 23 and 24, forming the cathodes, would normally be connected to a supply of coolant fluid. Also, the target electrodes 23 and 24 are separated by a water cooled earth screen 25 for the purpose of preventing inter-contamination of the electrodes.

A magnetic field in the order of 0.03 Tesla is established by electromagnets or periodically placed permanent magnets (not shown) which are positioned to extend in a direction approximately parallel to the target electrodes 23 and 24.

As is apparent from Figure 3, during rotation of the carrier 21 the glass tubes 10 are positioned between the target cathodes 23, 24 and the surrounding wall of the chamber 20. The glass tubes are thus exposed periodically to material that is sputtered from the target cathodes 23 and 24 as the material moves radially outwardly toward the surrounding chamber 20.

The target electrodes 23 and 24 are respectively formed from tungsten and aluminium. Metal is sputtered from the tungsten electrode 23 to form the infrared reflective layer 14 of the surface coating and, also, to form the metal fraction within the cermet layer 15 of the coating. Material is sputtered from the aluminium electrode 24 to form the dielectric fraction within the cermet layer 15.

In an alternative arrangement, metal might be sputtered from the aluminium element 23 to form the infrared reflective coating 14, particularly where high temperature thermal stability is not so important. As a further possible alternative, a third electrode, for example a copper electrode or a molybdenum electrode might be located within the chamber and be employed as a target electrode during deposition of the infrared reflective layer 14.

In forming the complete solar selective surface coating 13 on the tube 10, the chamber 20 is evacuated to a level in the order of 10^{-6} to 10^{-5} Torr. Argon gas is

then admitted to establish a pressure of 10^{-3} Torr and power is supplied to the tungsten electrode 23. Non-reactive dc magnetron sputtering occurs and tungsten is deposited substantially uniformly along the full length of the tubes 10. Sputtering is maintained for a time sufficient to achieve a coating thickness in the order of 300 nm. Each of the tubes 10 is rotated about its own axis and the carrier 21 is rotated about the chamber axis during the whole time that coating of the tubes is proceeding.

Having deposited the infrared reflective layer 14, the cermet layer 15 is formed by co-depositing material from both the tungsten and aluminium target cathodes 23 and 24 in the presence of a gas mixture containing both argon and nitrogen.

As stated previously, the tungsten is deposited as a metal fraction in the cermet composite, and the aluminium reacts with the nitrogen to form an aluminium nitride dielectric fraction in the cermet.

Tungsten is chosen as the preferred metal for use in the cermet layer 15 because it exhibits good oxidation resistance, is stable at room temperature and does not normally react with nitrogen gas at any temperature. However, when sputtering tungsten in a gas mixture which includes reactive nitrogen gas a small fraction of tungsten nitride may be formed and, in order to sputter a substantially pure tungsten metal phase into the cermet composite, the nitrogen partial pressure in the region of the tungsten cathode should be kept as low as possible.

In contrast with the nitriding resistance of tungsten, the chemical reactivity of aluminium with nitrogen is very high and it is relatively easy to nitride aluminium in the presence of nitrogen gas. Thus, aluminium sputtered from the cathode 24 is reactively sputtered with the nitrogen gas and a transition from the metal phase to the dielectric phase occurs as the nitrogen partial pressure is increased. With a relatively low nitrogen gas flow, the ratio of aluminium

to nitrogen is dependent upon the gas flow and aluminium in the metal phase will be deposited in the cermet. In order to deposit nearly stoichiometric aluminium nitride, a nitrogen gas flow rate is employed, using a gas flow controller (not shown), to establish a partial pressure of 10^{-4} Torr.

The co-deposition sputtering process is maintained in the presence of the nitrogen gas for such period of time as is required to establish a layer thickness in the order of 60 to 140 nm.

Finally, power to the tungsten cathode 23 is turned off and metal that is sputtered from the aluminium cathode 24 is reacted with the nitrogen to form a substantially pure aluminium nitride layer upon the cermet layer and so to form the anti-reflective layer 16. This process is maintained for sufficient time to establish a layer having a thickness in the order of 60 to 100 nm.

CLAIMS

1. A method of forming a solar selective surface coating which comprises the steps of -
 - (a) depositing an infrared reflective metal layer on a
 - 5 (b) depositing a solar energy absorptive coating in the form of a cermet on the reflective metal layer;wherein the cermet is formed by sputtering material simultaneously from first and second metal electrodes
- 10 onto the reflective metal layer in the presence of at least one gas which is reactive with the metal from which the second electrode is formed and substantially non-reactive with the metal from which the first electrode is formed.
- 15 2. The method as claimed in claim 1 wherein the metal from which the first electrode is formed is selected from the group comprising tungsten, tungsten based alloys, stainless steel, nickel, nickel based alloys, nickel-chromium alloys, platinum, iridium,
- 20 osmium, ruthenium, rhodium, rhenium, molybdenum, molybdenum based alloys and gold.
3. The method as claimed in claim 2 wherein the cermet is formed by sputtering the metal from the first and second electrodes in the presence of nitrogen gas and
- 25 an inert sputter supporting gas.
4. The method as claimed in claim 1 wherein the metal from which the first electrode is formed is selected from the group comprising platinum, iridium, ruthenium, rhodium, rhenium and gold.
- 30 5. The method as claimed in claim 4 wherein the cermet is formed by sputtering the metal from the first and second electrodes in the presence of oxygen and an inert sputter supporting gas.
- 35 6. The method as claimed in any one of claims 1 to 5 wherein the metal from which the second electrode is formed is selected from the group comprising aluminium and magnesium.

7. The method as claimed in claim 1 wherein the reflective metal layer is deposited as a metal selected from the group comprising aluminium, tungsten, copper, gold, silver and molybdenum.

5 8. The method as claimed in claim 1 wherein the metal from which the first electrode is formed comprises tungsten which is deposited to form both the infrared reflective metal layer and a metallic component of the cermet wherein the metal from which the second electrode
10 is formed comprises aluminium, and wherein the cermet is formed by sputtering the metal from the first and the second electrodes in the presence of nitrogen gas and an inert sputter supporting gas.

15 9. The method as claimed in claim 1 wherein the deposition of the infrared reflective metal layer and deposition of the cermet are effected by direct current or alternating current magnetron sputtering.

20 10. The method as claimed in claim 1 wherein the solar energy absorptive coating is deposited with a metal fraction of the cermet distributed substantially uniformly throughout a dielectric matrix of the cermet for substantially the full thickness of the coating.

25 11. The method as claimed in claim 1 wherein the solar energy absorptive coating is deposited with a metal fraction of the cermet distributed throughout a dielectric matrix of the cermet in a manner such that the metal fraction increases with increasing depth of the coating.

30 12. The method as claimed in claim 1 wherein the solar energy absorptive coating is deposited as a multi-layer cermet coating.

 13. The method as claimed in claim 12 wherein in adjacent ones of the multi-layer cermet coatings are deposited with different metal fractions.

35 14. The method as claimed in claim 13 wherein there are two only cermet coating layers, and wherein the inner layer cermet coating is deposited with a higher metal fraction than the outer layer cermet coating.

15. The method as claimed in claim 1 or claim 12 wherein the solar energy absorptive coating is deposited to a thickness which is substantially transparent to infrared radiation and which provides for absorption of solar radiation by internal absorption and phase cancellation interference.

16. The method as claimed in claim 15 wherein the solar energy absorptive coating is deposited to a thickness within the range 40 to 160 nm.

17. The method as claimed in claim 1 wherein the infrared reflective metal layer is deposited to a thickness in the range 100 to 400 nm.

18. The method as claimed in claim 1 wherein an anti-reflection surface layer in the form of a transparent dielectric material is deposited upon the solar energy absorptive coating.

19. The method as claimed in claim 18 wherein the anti-reflection surface layer is deposited as a composite selected from the group comprising aluminium nitride, aluminium oxide and aluminium oxynitride.

20. A solar selective surface coating that comprises an infrared reflective metal layer and a solar energy absorptive coating in the form of a cermet deposited on the reflective metal layer; wherein the absorptive coating is formed by sputtering material simultaneously from first and second metal electrodes onto the reflective metal in the presence of at least one gas which is reactive with the metal from which the second electrode is formed and substantially non-reactive with the metal from which the first electrode is formed.

21. A solar selective surface coating that comprises an infrared reflective metal layer and a solar energy absorptive coating deposited on the reflective metal layer; wherein the surface coating is deposited by the method as claimed in claim 1.

22. A solar selective surface coating that comprises an infrared reflective metal layer and a solar energy absorptive coating deposited on the reflective metal

layer; wherein the surface coating is deposited by the method as claimed in claim 8.

23. A solar collector element that comprises a tube through which a heat exchange fluid is in use passed, a glass envelope surrounding the tube, an evacuated space defined by the tube and the envelope, and a solar selective surface coating deposited on the outer surface of the tube; wherein the solar selective surface coating is deposited on the outer surface of the tube by the method as claimed in claim 1.

24. A method of forming a solar selective surface coating substantially as hereinbefore exemplified and described with reference to the accompanying drawings.

25. A solar selective surface coating substantially as hereinbefore exemplified when deposited by the method substantially as hereinbefore described with reference to the accompanying drawings.

26. A solar collector element substantially as shown in the accompanying drawings and substantially as hereinbefore described with reference thereto.

1/2

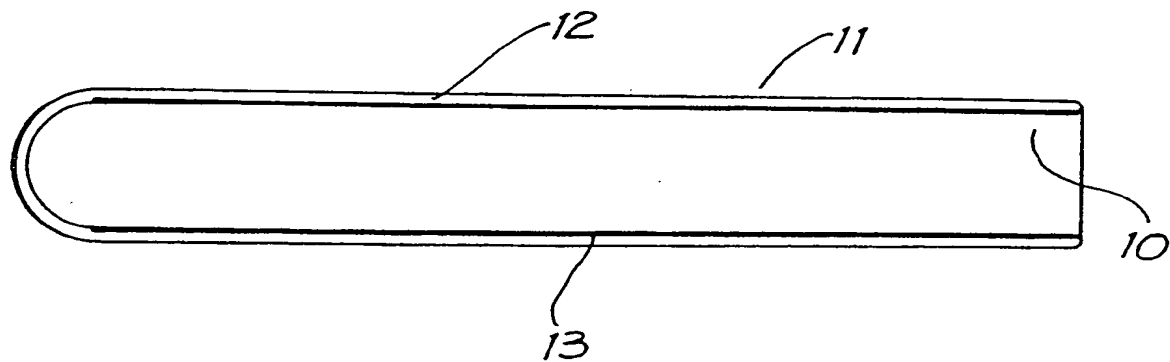


FIG. 1

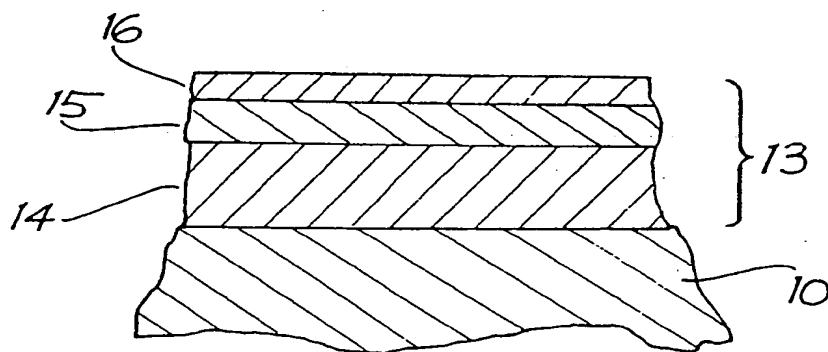
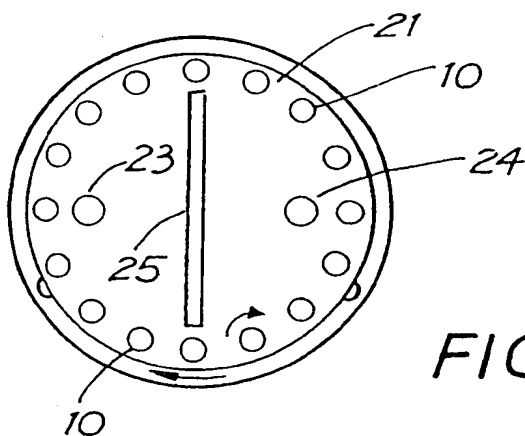
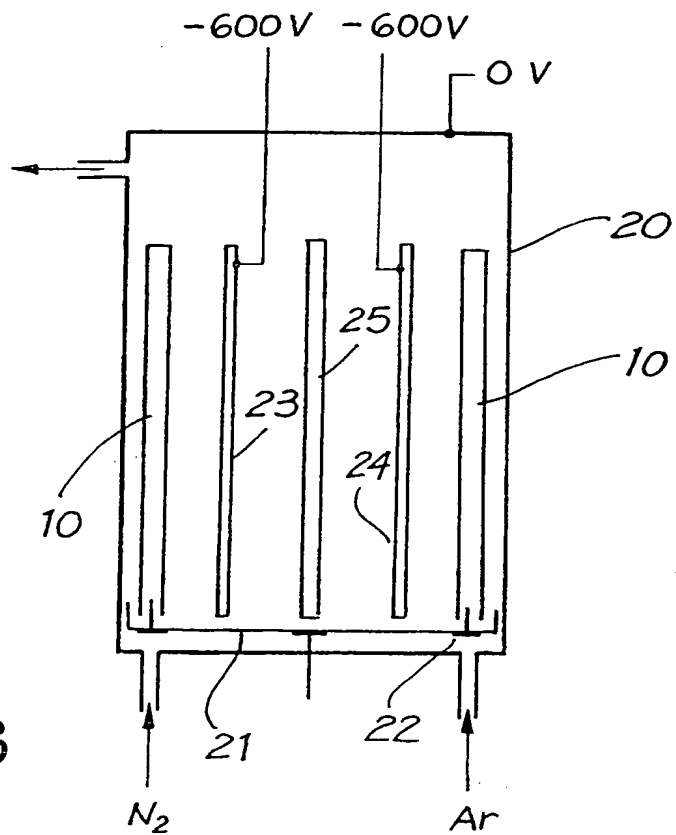


FIG. 2

2/2



INTERNATIONAL SEARCH REPORT

 International Application No.
 PCT/AU 96/00363
A. CLASSIFICATION OF SUBJECT MATTERInt Cl⁶: C23C 14/06 14/08 14/34 14/35 14/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 IPC C23C 14/06 14/08 14/34 14/35 14/36

 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 AU : IPC as above

 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 JAPIO : reflect: infrared: reactive: cermet: nitrit: oxide:
 WPAT: reflect: infrared: reactive: cermet: nitrit: oxide:
C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 4221864 A1 (VEGLA VEREINIGTE GLASSWERKE GmbH), 13 January 1994 See the abstract and examples	1-26
Y	WO 91/16197 A1 (CARDINAL IG COMPANY), 31 October 1991 See examples	1-26
A	EP 0104870 A2 (PILKINGTON BROTHERS P.L.C.) 04 April 1984 See the abstract and examples	1-26



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an

"Y"

 inventive step when the document is taken alone
 document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such

"&"

 combination being obvious to a person skilled in the art
 document member of the same patent family

Date of the actual completion of the international search

8 August 1996

Date of mailing of the international search report

19 AUG 1996

 Name and mailing address of the ISA/AU
 AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
 PO BOX 200
 WODEN ACT 2606
 AUSTRALIA Facsimile No.: (06) 285 3929

Authorized officer

SUDATH KUMARASINGHE

Telephone No.: (06) 283 2269

PCT/INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00363

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0007805 A1 (FUJITSU LIMITED), 6 February 1980 See the abstract and examples	1-26
A	DE 3628057 A1 (NIPPON SHEET GLASS CO,) 19 February 1987 See the abstract and examples	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/AU 96/00363

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
DE	4221864	NIL					
WO	91/16197	CA	2081341	US	5215832		
EP	0104870	AU	1928583	CA	1203197	DE	3375010
		DK	4314/83	DK	160758	EP	104870
		FI	833385	FI	77440	GB	8325063
		GB	2129831	JP	59076534	JP	5024987
		NO	833335	NO	157212	US	4462883
		ZA	8306920				
EP	0007805	DE	2964810	JP	55019854	JP	56028015
		US	4356210	US	4435443	JP	55075281
		JP	56035316				
DE	3628057	FR	2586245	JP	62041740	KR	9002707
		KR	8901994				
END OF ANNEX							